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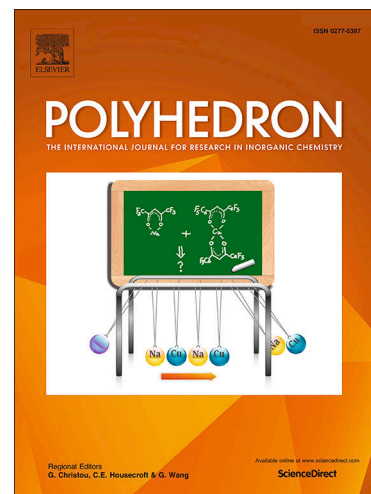
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Synthesis and Functionalization Reactivity of Fe-Thiocarbonyl and Thiocarbonyne Complexes

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Dedication: This article is dedicated to the memory of Professor Malcolm Green, FRS. I remember with fondness discussing the possibility of synthesizing terminal molecular carbide complexes with Malcolm some 25 years ago, and other fond memories with him in the years thereafter. He was a hero for so many of us “pot-boilers” in the field of organometallic chemistry.

Abstract

The remarkable catalytic transformation of CO to liquid hydrocarbons by Fe and Co catalysts in the industrial Fischer-Tropsch process motivates interest in developing well-defined systems to model aspects of this chemistry. One of the most interesting potential intermediates in this chemistry is a terminally-bound, first row metal carbide, yet a molecular model of this species remains elusive. With this in mind, we targeted the synthesis of highly-activated Fe-thiocarbonyl complexes, as prospective precursors to S-functionalization, C-S bond cleavage, and carbide generation. Herein, we describe the synthesis of three Fe-CS complexes that can be alkylated to generate a series of terminal Fe-carbynes that could be characterized across three oxidation states. Strategies to access C-S bond scission from these species are discussed, including limitations that, thus far, have precluded the generation of a terminal Fe-carbide for this system.

Introduction

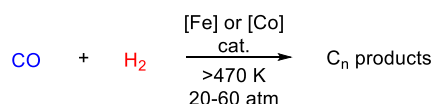
The industrial Fischer-Tropsch process mediates the reduction of CO with H₂ to generate liquid hydrocarbon products and is most frequently catalyzed by heterogeneous iron or cobalt species (Figure 1A).¹ In related reactivity, biological nitrogenase enzymes facilitate the proton-coupled reduction of CO to generate deoxygenated C-C coupled products (Figure 1B).² Both of these processes yield reduced hydrocarbons that are generated upon complete cleavage of the exceptionally strong C-O triple bond of carbon monoxide (256 kcal/mol), along with requisite C-H bond forming and C-C coupling steps. These transformations motivate interest in modeling aspects of CO functionalization and cleavage by well-defined complexes of Co³ and especially Fe.⁴ In this chemistry, one of the most intriguing plausible prospective targets for model studies is a terminally-bound iron or cobalt carbide,^{1,4,5} for which there are no reported molecular analogs.

To this end, we have developed phosphine-supported Fe systems that are able to support O-functionalization of sufficiently reduced Fe-CO complexes,⁶ including systems that are able to access well-defined C-C coupling⁷ and C-H bond forming steps (Figure 1C).⁸ To date, despite some effort, these systems have not been amenable to supporting complete C-O bond cleavage chemistry or the generation of a terminal carbide complex.⁹ This research builds upon foundational early work from Roper and co-workers, who modeled related aspects of Fischer-Tropsch reactivity using thiocarbonyl complexes of precious metals in groups 8 and 9.¹⁰ For iron-porphyrinoid systems, dihalocarbene complexes are readily accessed from CX₄ (X = Cl, Br) precursors.¹¹ Under similar reaction conditions, the use of Cl₄ led to the formation of a diiron-bridged carbide ligand.¹² In this chemistry, the intermediacy of a terminal carbide is plausible, but was not directly invoked. In fact, there are as of yet no reported examples of terminally-bound carbides of any first row transition metals and, as such, these species remain compelling synthetic targets.

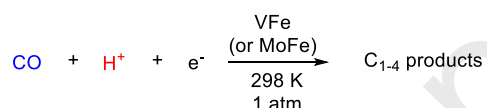
One of the primary barriers to the preparation of molecular metal carbides is a lack of generalizable approaches to their synthesis. The first reported synthesis of a terminal transition metal carbide that was achieved *via* deoxygenation of a Mo(CO) complex.^{13,14} An alternative synthetic approach provides access to this complex through application of a methyldiyne transfer

reagent that generates a metal-bound “C-H” fragment concurrent with the rearomatization of benzene.¹⁵ To extend these unusual structural motifs to group 8 systems, terminal Ru carbides were first prepared through olefin metathesis between Ru carbenes and reaction partners that serve as direct carbide precursors.¹⁶ Structurally-related terminal Ru and Os carbides are also accessible *via* S-atom abstraction from suitable metal-thiocarbonyl precursors.¹⁷ Subsequent work expanded upon this approach with the preparation of multinuclear metal carbides accessed via cleavage of thio- and selenocarbonyl precursors.¹⁸ To date, more general application of these and alternative approaches¹⁹ to carbide synthesis, especially for first row metal systems, remains to be realized.

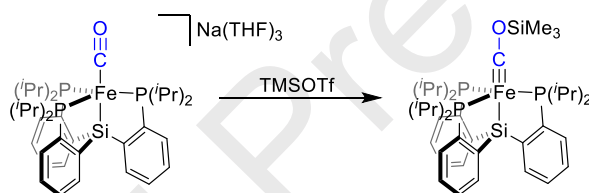
(A) Industrial Fischer-Tropsch Process



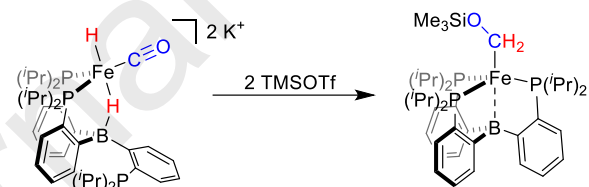
(B) Enzymatic CO Reduction by Nitrogenases



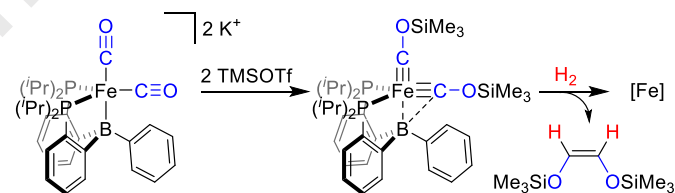
(C) CO Transformations by Fe Model Complexes
CO Functionalization



C-H Bond Formation



C-C Coupling



Elusive Target: CO Cleavage

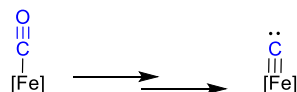
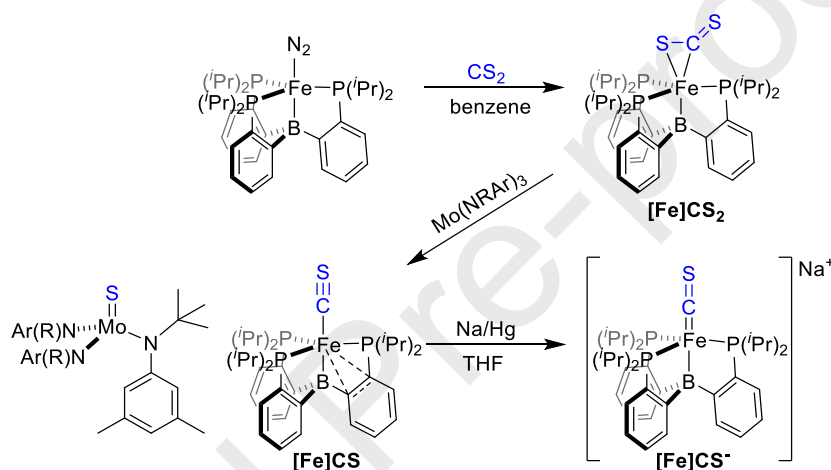


Figure 1. Industrial (A) and biological (B) processes that mediate deoxygenative reduction of CO to hydrocarbon products. (C) Transformations of CO mediated by phosphine-supported Fe-complexes.

In this report, we describe an effort targeting the synthesis of a terminal Fe-carbide complex. Given previous reports of C-O functionalization in Fe-carbonyl complexes, we hypothesized that moving to the corresponding thiocarbonyls might generate precursors amenable to S-functionalization reactivity and subsequent cleavage of the comparatively weak C-S bond.²⁰ To this end, we describe the synthesis of a series of Fe-CS complexes supported by a trisphosphine borane ligand. From a reduced state, S-alkylation reactivity is accessible, and provides access to a series of terminal thiocarbynes that are stabilized across three formal oxidation states. We then describe strategies that were explored to complete C-S bond cleavage in this system and limitations that prevented access to the targeted terminal iron carbide.

Results and Discussion

Synthesis and Characterization of Fe-CS Complexes



Scheme 1. Synthetic approach to generating $P_3^BFe(CS)$ complexes.

The system we initially targeted for the preparation of Fe-CS complexes was the P_3^BFe platform, $[Fe](P_3^B) (P_3^B = B(o\text{-}iPr_2PC_6H_4)_3)$.²¹ Previous work in our group has demonstrated that this system supports an array of stoichiometric N_2 functionalization chemistry,²² including complete N-N bond cleavage to generate a terminal Fe-nitride.²³ As such, we thought it might be a suitable starting point for exploring CS functionalization and cleavage chemistry.²⁴ Previous work demonstrated that bis- and tris(methimazoly)borane-supported thiocarbonyl complexes of Ru, Rh, and Ir could be accessed upon metalation of the boratrane ligands with suitable CS-ligated metal precursors.²⁵ Without a well-defined Fe-CS precursor for the present system, initial access to thiocarbonyl complexes for this system was provided by treating the previously reported $P_3^BFe-N_2$ complex²¹ with an equivalent of CS_2 to generate $P_3^BFe-CS_2$ $[Fe]CS_2$. The paramagnetically shifted 1H NMR spectrum of $[Fe]CS_2$ and its ^{57}Fe Mössbauer parameters are consistent with the formation of a new triplet species ($\delta = 0.44$ mm/s; $\Delta E_Q = 2.55$ mm/s). As a precursor to thiocarbonyl complexes on this platform, the CS_2 adduct $[Fe]CS_2$ could be generated cleanly *in situ* (Scheme 1) but decayed in solution over time to generate an intractable product mixture, precluding its clean isolation and structural characterization.

Motivated by the pioneering atom transfer reactivity displayed by $\text{Mo}(\text{NRAr})_3$,²⁶ treatment of the CS_2 adduct $[\text{Fe}]\text{CS}_2$ with an equivalent of $\text{Mo}(\text{NRAr})_3$ ($\text{R} = t\text{Bu}$; $\text{Ar} = 3,5\text{-dimethylphenyl}$)²⁷ in benzene led to the instantaneous darkening of the reaction solution.²⁸ NMR spectroscopic analysis of the resultant reaction mixture confirmed the formation of the previously reported $\text{Mo}=\text{S}$ complex²⁹ with concurrent formation of a new, diamagnetic Fe species, $\text{P}_3^{\text{B}}\text{Fe}(\text{CS})[\text{Fe}]\text{CS}$.³⁰ The similar solubility properties of these two products prevents their direct separation. Instead, reduction of the product mixture over an excess of Na/Hg amalgam in THF results in selective one-electron reduction of the Fe complex, which could then be isolated following crystallization as its Et_2O solvate $[\text{P}_3^{\text{B}}\text{Fe}(\text{CS})][\text{Na}(\text{Et}_2\text{O})_2][\text{Fe}]\text{CS}^-$ (40% yield from $\text{Fe}-\text{N}_2$; Scheme 1). Solid-state structural characterization of the Na-capped complex $[\text{Fe}]\text{CS}^-$ shows significant activation of the CS ligand (Figure 2). Specifically, the Fe-C bond distance of 1.703(2) Å is only slightly longer than typical Fe-carbynes^{31,32} (1.63-1.7 Å), suggesting that there is a significant contribution of Fe-to-C multiple bond character. Corresponding elongation of the C-S bond to 1.663(2) Å is observed, where this distance is appreciably longer than most structurally-characterized thiocarbonyl complexes (typically ~1.5-1.6 Å).³³ In solution, the paramagnetically-shifted ^1H NMR resonances of $[\text{Fe}]\text{CS}^-$ and its broad, axial EPR signature confirm it as an $S = 1/2$ metalloradical.

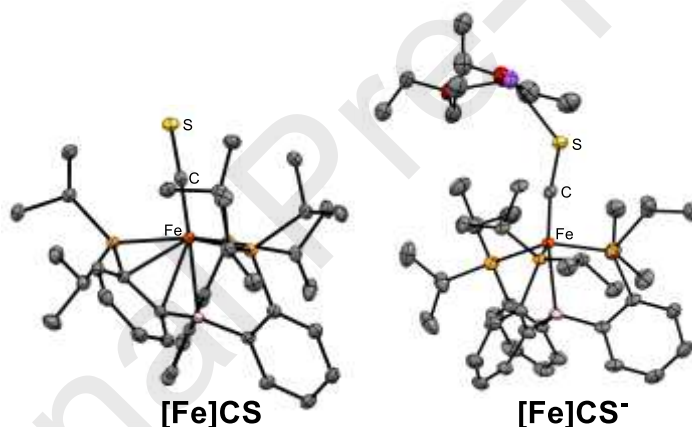


Figure 2. Crystal structures of the neutral and anionic thiocarbonyl complexes $[\text{Fe}]\text{CS}$ and $[\text{Fe}]\text{CS}^-$. Ellipsoids are shown at 50% probability with H-atoms omitted for clarity.

Reversible redox chemistry from $[\text{Fe}]\text{CS}^-$ can be accessed to generate two additional isolable thiocarbonyl complexes. Treating $[\text{Fe}]\text{CS}^-$ with $[\text{Cp}_2\text{Co}][\text{PF}_6]$ cleanly generates the neutral Fe-CS complex $[\text{Fe}]\text{CS}$ (Scheme 2). Like its corresponding Fe-CO complex, this species is diamagnetic, with an interaction observed in its solid-state structure between the Fe center and one of the phenylene linkers of the supporting ligand (Figure 2).²¹ Solution-phase three-fold symmetry is observed at room temperature, indicating that this interaction is fluxional on the NMR time scale. Bonding in the $[\text{Fe}-\text{CS}]$ unit of $[\text{Fe}]\text{CS}$ is fairly typical of transition metal thiocarbonyl complexes, with a C-S distance of 1.591(2) Å; the Fe-C distance in $[\text{Fe}]\text{CS}$ (1.734(2) Å) is slightly contracted relative to the isoelectronic Fe-CO complex (1.752(3) Å).²¹ Treating the anionic complex $[\text{Fe}]\text{CS}^-$ instead with an excess of KC_8 putatively generates the diamagnetic, dianionic thiocarbonyl complex $[\text{Fe}]\text{CS}^{2-}$ (Scheme 2). Efforts to structurally

characterize $[\text{Fe}]\text{CS}^{2-}$ have been unsuccessful to date and are complicated by its facile oxidation.³⁴

Characterization of this series of compounds by Mössbauer spectroscopy revealed that the most oxidized complex $[\text{Fe}]\text{CS}$ has an isomer shift of 0.14 mm/s and a quadrupole splitting of 1.89 mm/s (Figure 3). Sequential reduction events lower the isomer shift and contract the quadrupole splitting for complexes $[\text{Fe}]\text{CS}^{\cdot -}$ ($\delta = 0.09$ mm/s; $\Delta E_Q = 1.26$ mm/s) and $[\text{Fe}]\text{CS}^{2-}$ ($\delta = 0.03$ mm/s; $\Delta E_Q = 0.62$ mm/s). We and others have noted that the isomer shift trend observed for these phosphine-supported iron complexes is the opposite of the classical trend observed for species supported by hard donor ligands (e.g., N or O-atom donors). This has been attributed to contraction of the ligand field upon reduction of these species, which gives rise to increased s-electron density at the ^{57}Fe nucleus.³⁵ Interpretation of the observed trend in quadrupole splitting is complicated by the change in coordination geometry from $[\text{Fe}]\text{CS}$ to $[\text{Fe}]\text{CS}^{\cdot -}$ and $[\text{Fe}]\text{CS}^{2-}$, but suggests that there is lower asymmetry in the electric field gradient at the ^{57}Fe nucleus upon reduction.³⁶ These trends are consistent with the previously reported complexes $[\text{P}_3^{\text{B}}\text{Fe}(\text{N}_2)]^{0/1-/2-}$ and $[\text{P}_3^{\text{Si}}\text{Fe}(\text{CO})]^{+/0/-}$, albeit with smaller variance in the isomer shifts and quadrupole splittings for the thiocarbonyl complexes.^{6,22b,23}

S-Functionalization and Characterization of Thiocarbonyl Complexes

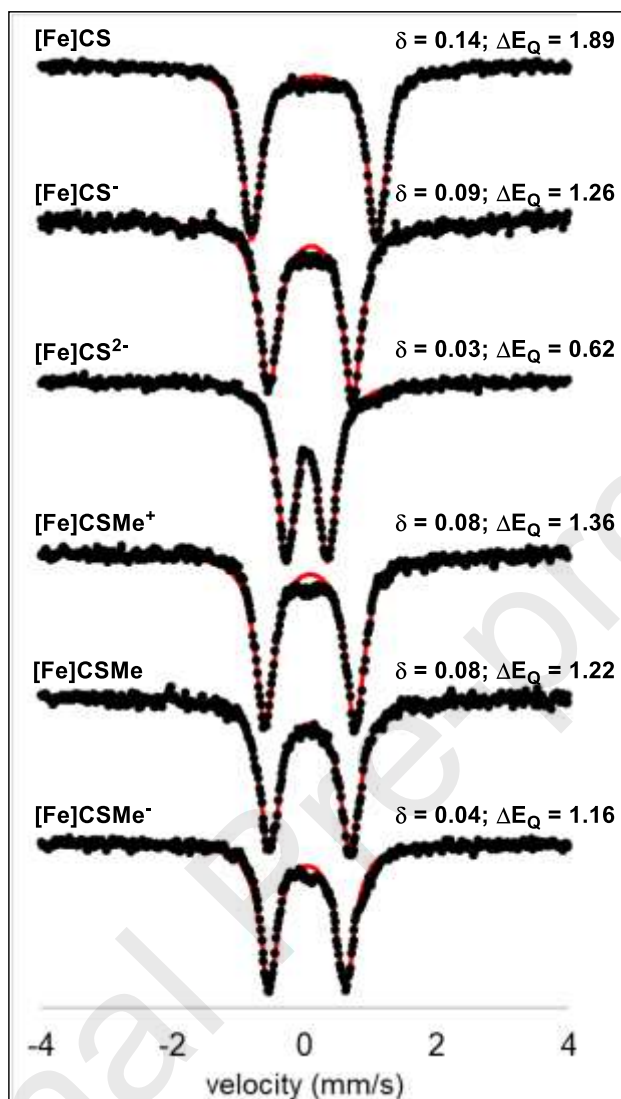
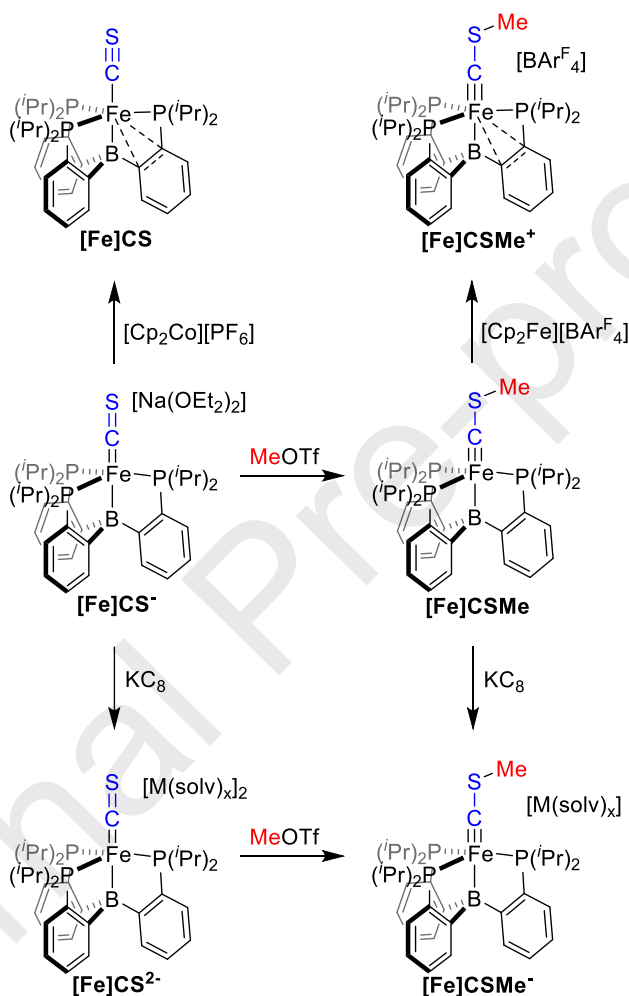


Figure 3. ^{57}Fe Mössbauer spectra of the thiocarbonyl and thiocarbene complexes.

Treating the anionic Fe-CS complex $[\text{Fe}]\text{CS}^-$ with an equivalent of MeOTf at low temperature led to the rapid consumption of the starting material (Scheme 2). The product of this transformation is a new doublet thiocarbene, with methyl group incorporation initially confirmed through the use of ^{13}C -labeled MeOTf.^{37,38} In the labeled product, strong ^{13}C -coupling is observed for the paramagnetically shifted ^1H NMR resonance associated with the incorporated methyl group. Structural characterization of the product confirmed its assignment. The structure of $[\text{Fe}]\text{CSMe}$ shows further activation of the C-S bond upon alkylation, with contraction of the Fe-C distance to 1.688(2) Å and elongation of the C-S distance to 1.706(2) Å (Figure 4). The contracted C-S-C angle of 103.4(1)° is comparable to previously reported thiocarbenes of Mo and W and is consistent with a relatively minor contribution of heteroatom π -stabilization for thiocarbene ligands.³⁹ Spectroscopically, complexes $[\text{Fe}]\text{CSMe}$ and $[\text{Fe}]\text{CS}^-$ are nearly indistinguishable, with remarkably similar EPR, NMR, and Mössbauer signatures (For

[Fe]CSMe: $\delta = 0.08$ mm/s; $\Delta E_Q = 1.22$ mm/s; Figure 3); this lends additional credence to the idea that the anionic thiocarbonyl complex **[Fe]CS⁻** has significant carbyne character.⁴⁰ When isolated in the solid state **[Fe]CSMe** is a thermally stable species, but was observed to slowly decompose in solution over time, undergoing loss of a methyl radical equivalent to regenerate the neutral thiocarbonyl complex **[Fe]CS**. We additionally note that complex **[Fe]CSMe** is an unusual example of a paramagnetic carbyne complex; closely related species have been described recently by our group.⁴¹



Scheme 2. Synthesis of thiocarbonyl and thiocarbene complexes over three oxidation states.

The one-electron oxidized carbyne complex could be accessed by stirring the neutral complex **[Fe]CSMe** with an equivalent of $[\text{Fc}][\text{BARF}_4]$ to generate dark green $[\text{P}_3^{\text{B}}\text{Fe}\equiv\text{C-SMe}][\text{BARF}_4]$ **[Fe]CSMe⁺** (Scheme 2). The methyl peak of the thiocarbene ligand is readily identified in the ^1H NMR spectrum of this complex with a sharp singlet resonance at 3.10 ppm. Characterization of this complex in the solid state shows only small perturbations to the bonding in the $[\text{Fe}\equiv\text{C-SMe}]$ unit upon oxidation (Figure 4), with very slight contraction of both the Fe-C (1.677(2) Å) and C-S (1.683(2) Å) distances in **[Fe]CSMe⁺** relative to its neutral precursor, and a similar C-S-C angle (103.9(1)°). Like the neutral thiocarbonyl complex **[Fe]CS**, an interaction between the Fe

center and one of the arene rings of the supporting ligand is observed in the solid-state structure of $[\text{Fe}] \text{CSMe}^+$; the symmetric NMR spectrum of $[\text{Fe}] \text{CSMe}^+$ again indicates that this interaction is fluxional in solution.

An anionic thiocarbonyl complex $[\text{Fe}] \text{CSMe}^-$ can be generated *in situ* upon reduction of $[\text{Fe}] \text{CSMe}$ (or $[\text{Fe}] \text{CSMe}^+$) with an excess of KC_8 at low temperature. This generates a single major diamagnetic product as identified by both NMR and Mössbauer spectroscopy. This complex can alternatively be accessed by alkylating the dianionic thiocarbonyl complex $[\text{Fe}] \text{CS}^{2-}$ with MeOTf (Scheme 2). $[\text{Fe}] \text{CSMe}^-$ is three-fold symmetric at low temperature in solution on the NMR timescale, consistent with rapid rotation around the C-S bond. In solution, $[\text{Fe}] \text{CSMe}^-$ is thermally unstable and, upon warming to room temperature, generates a product mixture that includes the anionic thiocarbonyl complex $[\text{Fe}] \text{CS}^-$. The thermal instability of $[\text{Fe}] \text{CSMe}^-$ has, to date, limited our ability to isolate this complex; attempts at structural characterization have yielded single crystals containing a mixture of the anionic thiocarbonyl $[\text{Fe}] \text{CSMe}^-$ and its decomposition product $[\text{Fe}] \text{CS}^-$ (see SI for details). The reactivity of this species when generated *in situ* is discussed below and provides additional circumstantial evidence for its assignment (see below).

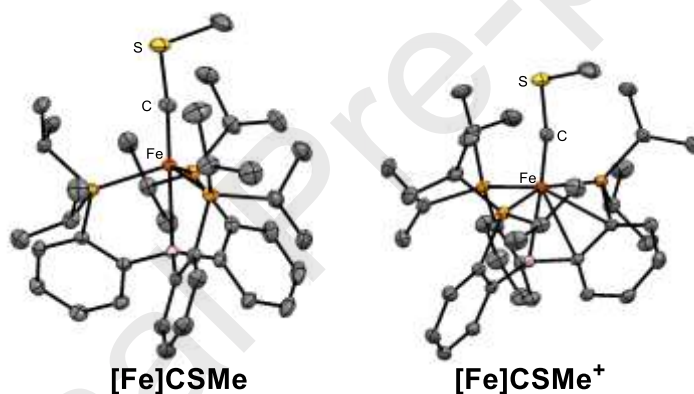


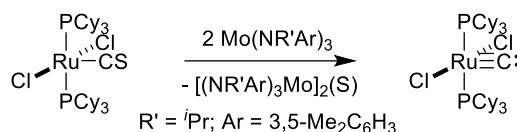
Figure 4. Crystal structures of $[\text{Fe}] \text{CSMe}$ and $[\text{Fe}] \text{CSMe}^+$ thiocarbonyl complexes. Ellipsoids are shown at 50% probability; H-atoms and the BARF_4 counteranion of $[\text{Fe}] \text{CSMe}^+$ are omitted for clarity.

To our knowledge, the characterization of a series of carbonyl complexes across three oxidation states is unique to this system.⁴² For this series, the ^{57}Fe Mössbauer spectra are remarkably invariant, with only a very slight decrease in the isomer shift observed upon reduction, from $\delta = 0.08$ mm/s in the cationic and neutral states $[\text{Fe}] \text{CSMe}^+$ and $[\text{Fe}] \text{CSMe}$ to 0.04 mm/s in the anionic complex $[\text{Fe}] \text{CSMe}^-$. Above, we noted the observed trends correlating metal-ligand distances and isomer shifts observed in structurally related phosphine-supported Fe complexes. The measured values for the thiocarbonyl complexes follow the same trend, with the narrow spread of values for both sets of complexes consistent with extensive metal-ligand covalency for these compounds. Concurrent with the decrease in the isomer shift is a very slight narrowing of the quadrupole splitting from $\Delta E_Q = 1.36$ mm/s for $[\text{Fe}] \text{CSMe}^+$ to 1.22 mm/s and 1.16 mm/s for

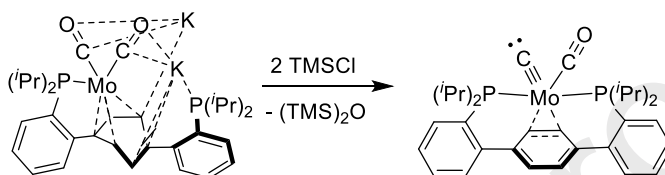
$[\text{Fe}] \text{CSMe}$ and $[\text{Fe}] \text{CSMe}^-$, respectively. Direct analysis of these values is complicated by the substantial structural distortion observed for the cationic complex $[\text{Fe}] \text{CSMe}^+$.

Exploring C-S Cleavage as a means to Terminal Carbide Generation

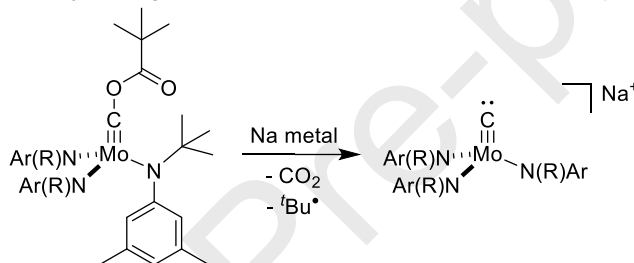
(A) S-Atom Abstraction



(B) CO Difunctionalization



(C) Carbyne Fragmentation



Scheme 3. Reported synthetic strategies for the synthesis of CO and CS-derived terminal transition metal carbides.

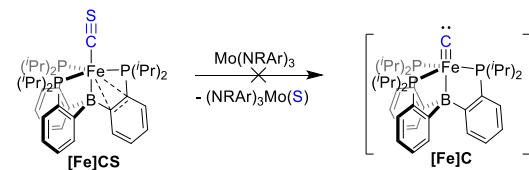
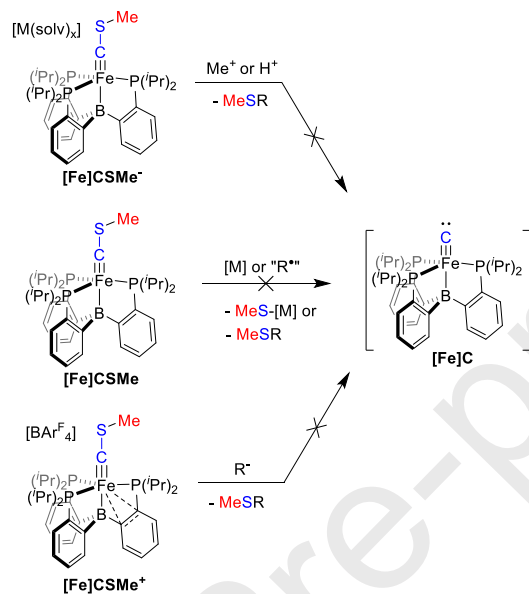
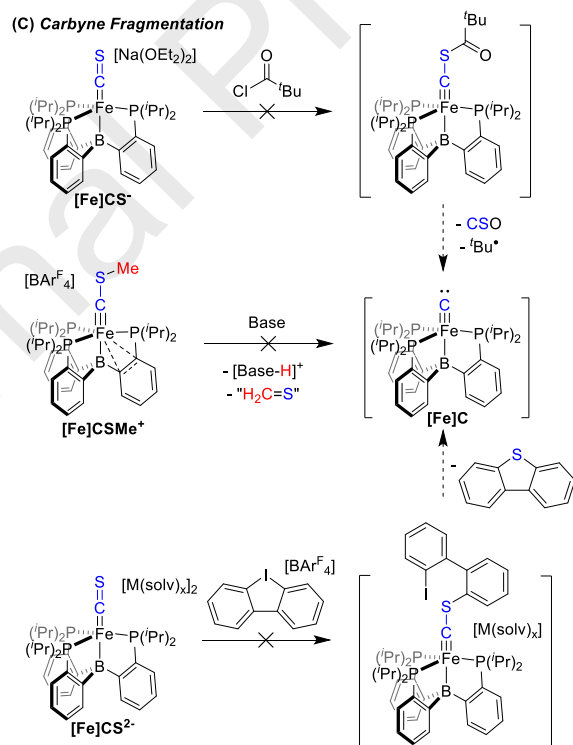
Our ability to access redox series of both the Fe-thiocarbonyl complexes and the S-functionalized carbyne complexes motivated us to pursue several parallel avenues toward accessing complete C-S bond cleavage. The terminal target of this reactivity was the neutral, diamagnetic iron carbide complex $\text{P}_3^{\text{B}}\text{Fe}(\text{C})$ ($[\text{Fe}] \text{C}$). As noted above, such a species would be the first terminal carbide complex of any first-row transition metal. Based on the significant precedent for the stabilization of complexes featuring strong M-to-L multiple bonds in three-fold symmetry for mid-to-late transition metal complexes, we anticipate that this species may have sufficient stability to be characterized. Previous theoretical investigations have examined the potential stability of five-coordinate Fe-carbide complexes, including $\text{Fe}(\text{CO})_4(\text{C})$, where the carbide ligand preferentially occupies one of the axial sites in the computed structures.⁴³ Computationally, the bonding of group 8 metals to carbide ligands is similar to what is proposed for Fischer-type carbenes, with the carbide ligand serving as an exceptional σ -donor and π -acceptor. More directly relevant to the targeted structure, work from our group has demonstrated the utility of the $\text{P}_3^{\text{B}}\text{Fe}$ platform for the stabilization of a number of species featuring strong M-L multiple bonds in the axial position *trans* to the anchoring boron atom. To date, species that have been accessed on this platform include imido²¹, hydrazido (2^-)²², and nitrido²³ complexes, in addition to the carbynes detailed in this work. The stability of these structure types has been

attributed, in part, to the unusual flexibility of the ligand platform along the Fe-B axis. At short Fe-B distances, this accommodates a trigonal bipyramidal geometry, where the Fe-B interaction helps stabilize highly reduced states that facilitate the binding and activation of π -acidic substrates.^{21a} Elongation of the Fe-B distance generates pseudotetrahedral structures that contribute to the stabilization of strongly π -basic ligands bound in the axial position.⁴⁴ Given the relative stability of these related P_3^BFe species and the predicted stability of $Fe(CO)_4(C)$, we hypothesized that **[Fe]C** would likely have sufficient stability to be characterized, provided a successful route to its generation could be realized.

To date, efforts to generate a terminal iron carbide from the described thiocarbonyl and thiocarbene complexes have been unsuccessful. One central obstacle to accessing a terminal carbide is the propensity for this system to engage in unproductive redox chemistry rather than the desired bond formation and cleavage reactivity. Nevertheless, the remaining discussion will outline some of the strategies that were considered and explored for the generation of **[Fe]C** from the thiocarbonyl and thiocarbene complexes discussed above. By elaborating these approaches, our hope is that one or more of these methods may be successfully applied in an alternative system or that the strategies described here will motivate improved approaches to carbide generation.

In this area, we began by targeting successful strategies that have been explored to form terminal carbides in other systems. One reported approach for the synthesis of terminal carbides of Ru^{16c} and Os^{17} was through direct S-atom abstraction reactivity. In these cases, treating $M(CS)$ complexes with S-atom abstracting reagents such as $Mo(NR^iAr)_3$ ²⁹ ($R = ^iBu$ or iPr ; $Ar = 3,5-Me_2C_6H_3$) or $Ta(OS^iBu)_3$ generates the desired Ru or Os carbides concomitant with the formation of the Mo and Ta sulfides (Scheme 3A).⁴⁵ To access the targeted neutral carbide **[Fe]C** via this approach, we explored S-atom abstraction from the charge neutral thiocarbonyl complex **[Fe]CS**. In solution, there is no detectable interaction between $Mo(NR^iAr)_3$ and **[Fe]CS**, with no conversion of **[Fe]CS** under any explored reaction conditions (Scheme 4A).

We subsequently considered approaches to C-S bond cleavage through derivatization of the synthesized thiocarbene complexes. Related reactivity has been reported where net difunctionalization of a reduced Mo-CO complex with silyl-chloride electrophiles generates an equivalent of disilylether and a terminal molybdenum carbide, with the reaction proceeding through a carbene intermediate (Scheme 3B).¹⁴ To extend this type of reactivity to our system, we envisioned a number of approaches to CS-difunctionalization reactivity to liberate a thioether (or thiol) and form the desired **[Fe]C** fragment. Our hypothesis here was that the reactivity accessible at S might be dictated by the overall charge or radical character of the Fe carbene complex.

(A) S-Atom Abstraction**(B) CS Difunctionalization****(C) Carbyne Fragmentation**

Scheme 4. Representative reactions pursued toward the synthesis of a terminal Fe-carbide complex.

To this end, we initially pursued the reactivity of $[\text{Fe}]\text{CSMe}^-$ toward additional alkyl or Brønsted acid electrophile equivalents (Scheme 4B). At low temperatures, this species was unreactive toward further S-functionalization, with unproductive redox chemistry observed upon warming or decay with net S-Me bond homolysis. To circumvent this limitation, we targeted reactivity of $[\text{Fe}]\text{CS}^-$ and $[\text{Fe}]\text{CS}^{2-}$ with alternative, tethered biselectrophiles such as the bistriflate $\text{TfO}(\text{CH}_2)_4(\text{OTf})^{46}$ and dibenzylidolium.⁴⁷ For these electrophiles, we hoped that productive, initial S-functionalization would generate intermediate species predisposed toward undergoing a second S-functionalization in an intramolecular fashion. Unfortunately, moving away from simple alkyl triflate/oxonium electrophiles ultimately resulted in little to no selectivity for productive S-functionalization. Exploring instead approaches to the derivatization of the radical complex $[\text{Fe}]\text{CSMe}$, we targeted approaches for the promotion of radical cleavage of the thiocarbonyne C-S bond. Treating $[\text{Fe}]\text{CSMe}$ with transition metal complexes reactive toward the cleavage of strong C-S bonds, including heterobimetallic Zr/Ir complexes developed by Bergman and co-workers,⁴⁸ vanadocene derivatives,⁴⁹ and a titanium tris-anilide complex developed by Cummins and co-workers, did not result in favorable reactivity.⁵⁰ Likewise, the *in situ* generation of C-centered radicals, formed upon photolysis of alkylcobaloximes, proved unfruitful.⁵⁰ Finally, the reactivity of the cationic carbyne $[\text{Fe}]\text{CSMe}^+$ with nucleophiles was examined, however for reagents where reactivity was observed, selectivity for one-electron reduction was favored over productive S-functionalization reactivity.

As a final approach to C-S bond cleavage and formation of $[\text{Fe}]\text{C}$, we targeted S-functionalization with alternative electrophiles that might be amenable to fragmentation to promote C-S bond cleavage following carbyne functionalization, akin to the strategy applied to generate the first example of a terminal transition metal carbide (Scheme 3C).¹³ Again, the poor selectivity for S-functionalization over net unproductive electron-transfer chemistry proved to be problematic and limited the utility of this type of approach for our system (Scheme 4C). Toward fragmenting the isolable thiocarbonyne, one could imagine a decomposition pathway where removal of a proton, H-atom, or hydride equivalent from the S-Me group would generate a reactive intermediate species poised to undergo fragmentation to form a thioformaldehyde equivalent and the targeted carbide species. This type of reactivity also proved to be inaccessible for this system.

Conclusions

In this report, we detailed the synthesis of a series of Fe-thiocarbonyl complexes supported by a trisphosphine ligand, which were targeted as prospective precursors to the generation of a terminal Fe-carbide. From a sufficiently reduced state, these complexes are amenable to S-functionalization with methyl triflate to generate a neutral, radical thiocarbonyne complex. This species accesses two redox events to generate a unique series of terminal metal carbynes stabilized across three formal oxidation states. To conclude we discuss a number of approaches that were explored to access complete C-S bond scission to generate a terminal carbide complex. Thus far, this reactivity has not been observed, but alternative avenues to the synthesis of first row metal carbides remain of interest in our group as part of our ongoing interest in modeling

Fischer-Tropsch reactivity. It is our hope that the synthetic approaches to terminal carbides outlined here motivate further efforts targeting these unusual species.

Experimental Section

General Considerations

All manipulations were carried out using standard Schlenk or glovebox techniques under an N₂ atmosphere. Solvents were deoxygenated and dried by thoroughly sparging with N₂ followed by passage through an activated alumina column in a solvent purification system by SG Water, USA LLC. Ethereal solvents (THF, Et₂O) were dried further by stirring over Na/K alloy (>2 h) and were filtered through Celite prior to use. Deuterated benzene was purchased from Cambridge Isotope Laboratories, Inc., and dried by refluxing over Ca-H then distilled and stored over Na metal. Deuterated THF was purchased from Cambridge Isotope Laboratories and dried over Na/K alloy and was filtered through Celite prior to use. Reagents were either purchased from commercial vendors and used without further purification unless noted or prepared according to published protocols.

Physical Methods

NMR spectra (¹H and ³¹P) were collected at room temperature (25 °C unless specified) on a Varian 400 MHz spectrometer, with low temperature data collected on a Bruker 400 MHz spectrometer. ¹H chemical shifts are reported in ppm, relative to tetramethylsilane using residual proton and ¹³C resonances from solvent as internal standards. ³¹P chemical shifts are reported in ppm relative to 85% aqueous H₃PO₄. X-band EPR spectra were obtained on a Bruker EMX spectrometer with the samples prepared in a 2-MeTHF glass. Mössbauer spectra were recorded on a spectrometer from SEE Co. (Edina, MN) operating in the constant acceleration mode in a transmission geometry. The sample was kept in an SVT-400 cryostat from Janis (Wilmington, MA). The quoted isomer shifts are relative to the centroid of the spectrum of a metallic foil of α -Fe at room temperature. Solution samples were prepared by freezing solutions in a Delrin cup in a glovebox with rapid transfer of frozen samples to a liquid nitrogen bath before mounting in the cryostat. Samples were collected with no applied magnetic field unless otherwise specified. Data analysis was performed using the program WMOSS (www.wmoss.org) and quadrupole doublets were fit to Lorentzian lineshapes.

X-Ray diffraction and combustion analysis measurements were carried out in the Beckman Institute Crystallography Facility. XRD measurements were collected using a dual source Bruker D8 Venture, four-circle diffractometer with a PHOTON II detector or a Bruker D8 KAPPA with a PHOTON 100 detector. Structures were solved using SHELXT and refined against F^2 on all data by full-matrix least squares with SHELXL. The crystals were mounted on a glass fiber under Paratone N oil. See below for any special refinement details for individual data sets. Combustion analysis measurements were collected using a PerkinElmer 2400 Series II CHN Elemental Analyzer by facility staff.

Synthetic Details

[P₃^BFe(CS)][Na(Et₂O)] *In situ* generation of **[Fe]CS₂** was carried out by adding CS₂ (5 M in THF; 1.05 equiv, 65 μ L, 0.328 mmol) to a solution of P₃^BFe(N₂) (210.4 mg, 0.312 mmol) in benzene (7 mL), which yielded a red solution after stirring at room temperature for 20 min. This solution was then transferred to a second vial containing Mo(NR_{Ar})₃ (1.05 equiv, 204.6 mg, 0.328 mmol) and the resultant solution was stirred for an additional 30 min, turning dark brown. The solvent was removed *in vacuo* and the residue was redissolved in THF (7 mL) and stirred vigorously over an excess of Na/Hg amalgam for 1 h, giving a dark red-brown solution. This solution was decanted away from the residual Na/Hg and the solvent was removed *in vacuo*, leaving a dark residue. The residue was triturated and then washed with pentane until the washes were colorless or slightly yellow. The residue was then extracted into Et₂O, concentrated, and then layered with pentane at -30 °C to yield the product as a dark crystalline solid (107.2 mg; 40% from P₃^BFe(N₂)). ¹H NMR (C₆D₆, 400 MHz): δ 16.33, 14.19, 10.83, 7.06, 5.10, 4.80, -1.62, -2.34. ⁵⁷Fe Mössbauer (powder, 80 K): δ = 0.09 mm/s; ΔE_Q = 1.26 mm/s; Γ_L = 0.37 mm/s/ Γ_R = 0.34 mm/s. Anal. Calcd. for C₄₅H₇₄BFeNaO₂P₃S: C, 62.72; H, 8.66; N, 0.00. Found: C, 62.68; H, 8.17; N, <0.5.

P₃^BFe(CS) The thiocarbonyl complex **[Fe]CS** was initially generated as the primary product of desulfurization of **[Fe]CS₂** by Mo(NR_{Ar})₃ as an intermediate in the synthesis of **[Fe]CS⁻**. The same species could be generated cleanly Fe-containing *via* one electron oxidation of **[Fe]CS⁻** in THF using [Cp₂Co][PF₆]. The similar solubilities of **[Fe]CS** and Cp₂Co precluded their complete separation, but materials generated using this method were used for solution phase characterization of **[Fe](CS)**. Single crystals of this material suitable for characterization by XRD could be generated by slow evaporation of a pentane solution into MeCy. ³¹P{¹H} NMR (C₆D₆, 162 MHz): δ 74 (very br). ¹H NMR (C₆D₆, 400 MHz): δ 7.45 (d, J = 7 Hz, 3H), 7.37 (d, J = 7 Hz, 3H), 7.15 (overlapping benzene, 3H), 7.01 (t, J = 7 Hz, 3H), 2.85 (br, 6H), 1.74 (br, 9H), 1.55 (br, 9H), 1.07 (br, 9H), 0.63 (br, 9H). ⁵⁷Fe Mössbauer (benzene solution, 80 K): δ = 0.14 mm/s; ΔE_Q = 1.89 mm/s; Γ_L/Γ_R = 0.34 mm/s.

[P₃^BFe(CS)][M₂(solv)_x] The high reactivity of this complex precludes its reliable isolation and has limited our ability to structurally characterize this species. For solution phase characterization, solutions of **[Fe]CS** or **[Fe]CS⁻** were dissolved in THF and stirred with an excess of KC₈ at -78 °C in the glovebox coldwell. Excess reductant and graphite could be removed by filtration leaving dark brown/black solutions of the dianionic complex **[Fe]CS²⁻**. Partial solution phase decomposition of this species is apparent from the presence of metal-free ligand decomposition products in the NMR spectra (see Supporting Information) as well as minor hydride containing species. The extremely reactive nature of this complex resulting in its solution phase decomposition has hindered our efforts to isolate it in the solid state and precludes combustion analysis; this decomposition also gives rise to broad features in the ¹H NMR spectrum, which we attribute to a rapid redox equilibrium with a paramagnetic impurity (likely one-electron oxidized **[Fe]CS⁻**). The Mössbauer data, in particular, suggests that *in situ* generation of **[Fe]CS²⁻** yields a major Fe-containing product, consistent with our proposed assignment. ³¹P{¹H} NMR (THF, 162 MHz): δ 93.0. ⁵⁷Fe Mössbauer (THF solution, 80 K): δ = 0.03 mm/s; ΔE_Q = 0.62 mm/s; Γ_L/Γ_R = 0.33 mm/s.

P₃^BFe≡CSMe A dark orange solution of **[Fe]CS[•]** (49.7 mg, 0.0924 mmol) was prepared in THF (3 mL) and stirred at -78 °C in the glovebox coldwell. To this prechilled solution, MeOTf (10.6 μL, 0.0970 mmol, 1.05 equiv) was added *via* syringe, resulting in an immediate darkening of the solution. After stirring at -78 °C for 10 min, the solution was warmed to room temperature and the solvent was removed *in vacuo*. The residue was triturated with pentane and then extracted into benzene, yielding the product as a brown powder upon lyophilization (49.7 mg, 76%). Single crystals of this material suitable for characterization by XRD could be generated by slow evaporation of a pentane solution into MeCy. ¹H NMR (400 MHz, C₆D₆) δ 16.09, 12.32, 10.22, 4.45, 2.18 -1.05, -2.89, -3.64, -6.09. ⁵⁷Fe Mössbauer (powder, 80 K): δ = 0.08 mm/s; ΔE_Q = 1.22 mm/s; Γ_L/Γ_R = 0.38 mm/s. Anal. Calcd. for C₃₈H₅₇BFeP₃S: C, 64.69; H, 8.14; N, 0.00. Found: C, 63.79; H, 8.00; N, <0.6.

[P₃^BFe≡CSMe][BAr^F₄] A solution of **[Fe]CSMe** (32.5 mg, 0.046 mmol) was prepared in 2:1 Et₂O/THF (2 mL) and cooled to -78 °C in the glovebox coldwell. A similarly prechilled solution of **[Fc][BAr^F₄]** (0.95 equiv, 45.9 mg, 0.044 mmol) in Et₂O/THF (2 mL) was added and the mixture was stirred at -78 °C for 1 h. The solvent was removed *in vacuo* and the resultant residue was washed with pentane and then benzene until the washes were colorless. The resultant green residue was extracted into a 1:1 Et₂O/THF mixture, giving the desired product **[Fe]CSMe⁺** as a dark green powder following solvent removal. The product could be obtained as a crystalline solid by layering a THF solution of the product with pentane at -30 °C (50.5 mg; 70%). No ³¹P resonance is observed for this species at room temperature; we attribute this to equilibration of the Fe-arene interaction. ¹H NMR (400 MHz, THF-*d*₈): δ 7.86 – 7.76 (s, 8H, BAr^F₄), 7.71 (t, *J* = 6.8 Hz, 3H), 7.57 (s, 4H, BAr^F₄), 7.53 (overlapping, 3H), 7.45 (t, *J* = 7.1 Hz, 3H), 7.25 (d, *J* = 7.7 Hz, 3H), 3.10 (s, 3H, SMe), 2.77 (br, 3H), 1.66-1.59 (overlapping, *J* = 14.7, 14.0, 7.2 Hz, 18H), 1.00 (dd, *J* = 15.2, 6.8 Hz, 9H), 0.78 (br, 3H), 0.64 (dd, *J* = 13.1, 6.4 Hz, 9H). ⁵⁷Fe Mössbauer (powder, 80 K): δ = 0.08 mm/s; ΔE_Q = 1.36 mm/s; Γ_L/Γ_R = 0.35 mm/s. Anal. Calcd. for C₇₀H₆₉B₂F₂₄FeP₃S: C, 53.60; H, 4.43; N, 0.00. Found: C, 52.98; H, 4.39; N, < 0.1.

[P₃^BFe≡CSMe][K(solv)_x] Solutions of **[Fe]CSMe[•]** were typically prepared by *in situ* reduction of **[Fe]CSMe** with an excess of KC₈ in THF at -78 °C. For NMR and Mössbauer characterization, **[Fe]CSMe** was directly reduced in THF or THF-*d*₈ to generate a solution of **[Fe]CSMe[•]**. For Mössbauer spectroscopy, samples were reduced directly in the sample holder and collected without removal of excess reductant. Single crystals of a mixture of **[Fe]CSMe[•]** and **[Fe]CS[•]** were prepared by reducing concentrated solutions of **[Fe]CSMe** in THF, filtering the resultant mixture to remove excess reductant, and layering the resultant solution with pentane at -30 °C. Warming solutions of **[Fe]CSMe[•]** to room temperature led to the rapid decolorization of the dark red solutions to yield orange solutions containing **[Fe]CS[•]**, generated upon loss of a methyl radical equivalent. ³¹P{¹H} NMR (400 MHz, THF-*d*₈): δ 98.5. ¹H NMR (400 MHz, THF-*d*₈): δ = 7.14 (Ar C-H, 3H), 6.95 (Ar C-H, 3H), 6.64 (Ar C-H, 3H), 6.48 (Ar C-H, 3H), 2.55 (*i*Pr C-H, 6H), 2.37 (S-Me, 3H), 1.23 (*i*Pr CH₃, 9H), 1.10 (*i*Pr CH₃, 9H), 0.90 (*i*Pr CH₃, 9H), -0.33 (*i*Pr CH₃, 9H). ⁵⁷Fe Mössbauer (THF solution, 80 K): δ = 0.04 mm/s; ΔE_Q = 1.16 mm/s; Γ_L/Γ_R = 0.35.

Appendix A. Supplementary data

CCDC 2089685-2089689 contains the supplementary crystallographic data for **[Fe]CS**, **[Fe]CS[•]**,

[Fe]CSMe, [Fe]CSMe⁺, and [Fe]CSMe⁻. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Declaration of interests

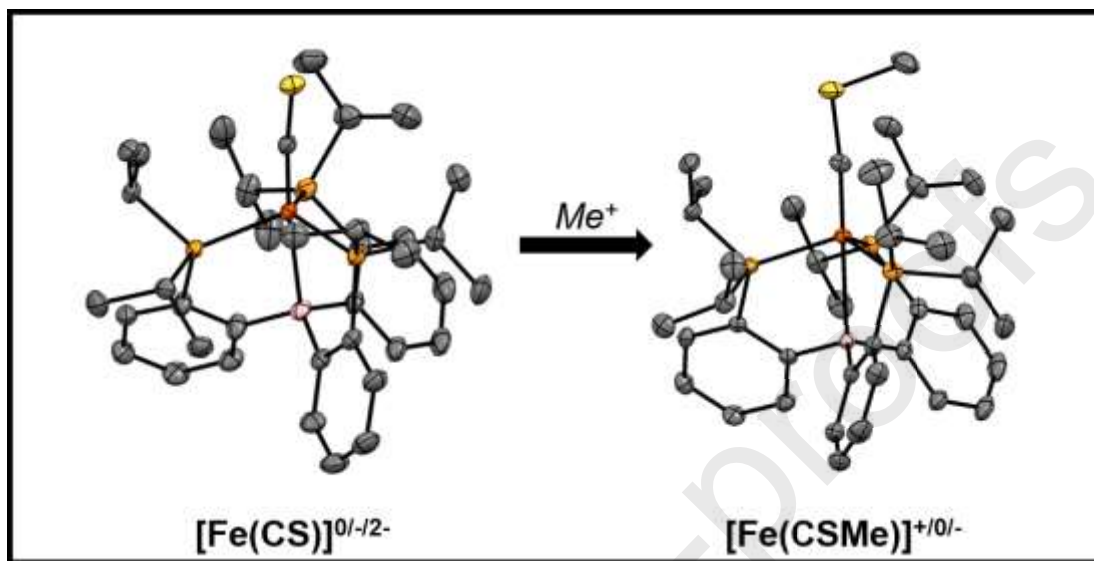
☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Meaghan Deegan, PhD - *Conceptualization; Data curation; Formal analysis; drafting of manuscript*

Jonas Peters, PhD - *Conceptualization; Formal analysis; drafting of manuscript*

TOC Graphic and Synopsis



We report the synthesis and characterization of a structurally-related series of iron-thiocarbonyl and methyl-functionalized iron-thiocarbonyl complexes. Strategies towards the conversion of these species to a terminal iron carbide are also discussed.